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PATENT SPECIFICATION

DRAWINGS ATTACHED

949,968

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Date of Application and filing Complete Specification March 3, 1960.

No. 7603/60.

Application made in United States of America (No. 798,959) on March 12, 1959.

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International Classification:—C 08 g (C 08 f g j)

COMPLETE SPECIFICATION

Expanded Polymer Particles and Process for their Production

PATENTS ACT, 1949

SPECIFICATION NO. 949,968

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 19th March 1968 this Specification has been amended under Section 14 in the following manner:—

Page 5, line 82, delete "which is substantially below 1 g/c cm." insert "of 0.0018 gm./cc or lower"

Page 5, lines 85 and 86, delete "corresponding approximately to that of air." insert "the same as the density of air."

Page 5, line 120, after "39" insert "and using a gas stream at a velocity close to or higher than sonic velocity"

THE PATENT OFFICE,
21st August 1968

D 105148/2

... enough to initiate the foaming or expansion of the polymeric material introduced or formed, and a velocity which is close to or higher than sonic velocity.

30 The velocity of the gas stream may be increased at the point where the reactants or the polymeric material are introduced into the gas stream by reducing the cross-section of the gas stream such as by insertion of a venturi into the path of the gas stream, whereby it is
35 of advantage to introduce the reactants or the polymeric materials, respectively, at or near the narrow passageway. It is of further advantage to give the gas stream a high rate of turbulence at or near this point.

40 The expanded polymeric particles produced by the process according to the invention are open or closed cell micro particles with a

highly divided and dispersed in the polymer making up the cell walls. The particles have generally a density which is substantially below that of the artificial fogs or smokes known
70 hereinbefore, i.e. below 1 g/c cm, and preferably of the order of the density of air or lower. The unusually low density of the micro particles of the invention makes them eminently suitable to be dispersed in a gas
70 such as air, wherein they form a fog or smoke having an unusually low settling rate.

The starting materials for the process may be any desired polymeric materials, and particularly synthetic polymers which preferably
80 contain a suitable blowing agent, for instance, one which is effective by thermodecomposition with the formation of gaseous decomposition products or by the expansion of a gas or



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International Classification:—C 08 g (C 08 f g j)

COMPLETE SPECIFICATION

Expanded Polymer Particles and Process for their Production

- I, BETTY LOU RASKIN, a Citizen of the United States of America, of 6221, Greenspring Avenue, Baltimore, County of Baltimore, State of Maryland, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a process and apparatus for making polymeric materials and to the material produced thereby.
- According to the invention, there is provided process for the production of an expanded, particulate organic polymeric material which comprises introducing or injecting a polymeric material or, if desired, suitable starting materials or reactants which are capable of forming such polymeric material, and which polymers or starting materials, respectively, are, due to their composition or due to the presence of a suitable adjuvant, capable of foaming or expanding at an elevated temperature, into a stream of a hot gas which has a temperature high enough to initiate the foaming or expansion of the polymeric material introduced or formed, and a velocity which is close to or higher than sonic velocity.
- The velocity of the gas stream may be increased at the point where the reactants or the polymeric material are introduced into the gas stream by reducing the cross-section of the gas stream such as by insertion of a venturi into the path of the gas stream, whereby it is of advantage to introduce the reactants or the polymeric materials, respectively, at or near the narrow passageway. It is of further advantage to give the gas stream a high rate of turbulence at or near this point.
- The expanded polymeric particles produced by the process according to the invention are open or closed cell micro particles with a size of between 1 and 1,000 microns. Ease of manufacture and the adaptability in the control of the physical properties of the particles in any desired manner, place the preference on synthetic thermoplastic or thermosetting addition or condensation polymers e.g. urea-formaldehyde polymers, phenolic condensation polymers, polyurethane resins, epoxy resins or silicone resins. The individual particles may be composed of open or closed cells or they may have both kinds of cells, and each particle may be made up of one individual cell or of an association or aggregation of cells. The number of the cells making up the aggregate is preferably relatively small. The closed cells or units may be filled with a gas such as air, nitrogen, carbon dioxide or helium, or any other gas, or with an inorganic or organic vapour such as that of acetone, methyl chloride or other halogenated lower hydrocarbons.
- The micro particles of the invention may contain fillers or additives such as pigments or finely divided metal particles, e.g. aluminium flake, which additives are preferably finely divided and dispersed in the polymer making up the cell walls. The particles have generally a density which is substantially below that of the artificial fogs or smokes known hereinbefore, i.e. below 1 g/c cm, and preferably of the order of the density of air or lower. The unusually low density of the micro particles of the invention makes them eminently suitable to be dispersed in a gas such as air, wherein they form a fog or smoke having an unusually low settling rate.
- The starting materials for the process may be any desired polymeric materials, and particularly synthetic polymers which preferably contain a suitable blowing agent, for instance, one which is effective by thermodecomposition with the formation of gaseous decomposition products or by the expansion of a gas or

volatile liquid contained on or in the polymeric material. The polymers may be thermoplastic or thermosetting. If desired, one may employ as the starting material reactants which unite to form the polymeric material upon contact within the gas stream. The expansion of the polymer thus formed in the process may be brought about by the presence of suitable blowing agents or by the formation of gases or vapors as a result of the chemical reaction taking place such as is the case with the foaming polyisocyanate reactants or prepolymer compositions. Depending on the properties and nature of the polymeric material introduced or formed in the gas stream, it may be desirable that the polymer is hardened or cured in the expanded form. The hardening may be effected or accelerated by the presence of catalysts, cross-linking agents, or similar adjuvants, and/or by the effects of the high temperature employed in the process.

If it is desired to utilize the expanded micro particles of the present invention directly for the formation of stable smoke or fog, or other aerosol, the gas stream producing the expanded polymeric materials may be directly blown into space or into the atmosphere. The expanded micro particles may serve as a carrier for a multitude of materials, and particularly for biologically active materials such as insecticides. The size and the density of the particles may be controlled by varying the temperature and the relative volume and/or the velocity of the hot gas stream. The size and the density of the particles may be furthermore controlled by the selection of the blowing agent and by adjusting the ratio of blowing agent to polymeric material.

If the polymer is used in liquid form or in the form of a solution as the case may be, it may be injected in one or several independent streams into the hot gas stream. If the polymer is formed in the gas stream by the reaction of two or more components capable of reacting with each other to form the polymer, the components are generally injected into the hot gas stream separately as individual streams.

As has been shown hereinbefore, the finely divided expanded polymeric particles of the invention may be readily and economically produced in a wide range of particle sizes and particle densities by injecting a foam-forming polymeric composition into a stream of gas at a temperature above the foam-developing temperature of the plastic composition.

The individual particles may be separated from the dispersions of the particles and the carrier gas as they are obtained in the process of the invention by suitable means.

The method of the invention not only makes it possible to vary the size and the density of the dispersed particles independently over wide ranges, which is an outstanding advantage

over methods heretofore available, but it also permits other characteristics of the particles such as color, surface reflectance and hygroscopicity to be varied independently of the size and density of the particles.

The expanding or blowing component of the foam-forming compositions may be added to the polymeric compositions as such; it may be generated by a condensation reaction between components of the polymeric composition; or it may be generated by the reaction of components added to the composition for this purpose alone.

The novel process of the present invention may employ any type of polymeric material which is capable of being produced as, or being converted to, a foam-forming composition, some types in a variety of ways, and this fact greatly adds to the adaptability of the invention to a wide variety of uses. For example, agents which expand by evaporation, such as water, acetone, methyl chloride and other chlorinated and/or fluorinated lower hydrocarbons, or agents which decompose on heating with the formation of gases, such as organic azo and nitroso compounds are particularly useful in imparting foaming properties to thermoplastic and thermosetting compositions such as polyvinyl chloride phenol-formaldehyde resins, polyurethane resins and polystyrene. The organic isocyanates are also useful foaming agents in various types of plastic wherein they react, for example, with alcoholic or carboxylic acid components, with the formation of carbon dioxide. Instead of, or in addition to, the agents mentioned above, air or other gas such as helium may be whipped into a polymeric composition, such as phenol-formaldehyde resins or polyvinyl chloride, which is then injected into the hot gas stream where it is hardened by the action of the heat of the gas stream, which may be aided by the addition of a catalyst. The foaming agents may also be injected into the polymeric compositions or a portion thereof in the conduit by which they are conveyed into the hot gas stream.

Filler and pigment components will usually be omitted from the compositions for the purpose of the present invention, but fillers and pigments, as well as other ingredients, may be added to the compositions to vary the properties of the dispersed particles for particular purposes. For example, finely divided flake metallic pigments, such as aluminium flake, may be added to vary the reflectance of the particles of smoke or fog containing the particles to light or other radiation.

The stream of hot gases into which the foam-forming plastic compositions are injected may be provided in a variety of ways. Gas turbines, including the portable type, provide a very advantageous source of hot gases for use in making plastic aerosols by the method

of the invention at any desired location. However, exhaust gases from internal combustion engines, jet, turbojet and rocket motors may be used. The source and nature of the hot gas stream is generally not important except as a matter of convenience and economy. Generally, it is also preferred to employ a gas which is substantially inert, under the processing conditions, to the polymer or the reactants and adjuvants used.

Typically, the foam-forming plastic composition is injected into the hot gas stream in liquid form, either in a single stream or in two or more streams each containing different components of the foam-forming composition. According to the character of the composition, normally solid compositions or components may be liquefied by warming, by adding volatile solvents thereto, or a liquid or finely divided solid composition may be dispersed in a carrier liquid or gas and injected or blown into the hot gas stream.

The polymeric particles may be separated from the carrier gas by any of a variety of means such as centrifugal or cyclone separators, bag filters or electrical precipitators. The choice of separating devices will depend to some extent on the character of the particles and of the carrier gases but in general the type of separator will not be critical.

The accompanying drawing is a diagrammatic representation of apparatus suitable for use in practising the method of the invention.

In the drawing, 10 is a compressor and 11 is a turbine on the same shaft therewith, with a combustion chamber 12 heating compressed air from the compressor on the way to the turbine in accordance with the common arrangement. Hot exhaust gases from the turbine pass through venturi 13. 14 and 15 are tanks for containing liquid foam-forming polymeric compositions or components thereof. Tanks 14 and 15 are supplied with compressed air through line 18 which serves to force the contents of the tanks through lines 16 and 17 into venturi passage 13 wherein the compositions are brought to foaming temperature and are converted into dispersion of fine particles of foamed polymer.

The density of the dispersed particles can be varied by varying the nature and proportion of the polymer composition and the blowing agent, the reaction temperature and other variables. It is possible to produce aerosols in which the density of the dispersed plastic particles is as low as or lower than that of air (0.0012 gm/cc). This makes possible the production of smokes of low fall-out rates with particles of relatively large size. For example, a phenol-aldehyde foam smoke of ten micron diameter particles having a density of 0.0016 gm/cc has a theoretical setting rate of only 1.7 cm/hr., while a fog oil smoke composed of one micron diameter particles of 2 gm/cc

density has a theoretical setting rate of 21.6 cm/hr.

While the temperature and relative volume of the hot carrier gas stream are not critical as long as the temperature and velocity is high enough to affect a rapid expansion, both of these variables affect the size and density of the particles. By variation of the temperature and volume relationships, design of the injection nozzles, and the character and amount of the blowing agents, it is possible to vary the size and density of the particles over a wide range. The average particle size may be varied from 1 micron to 1000 microns, and the cells may be open or closed according to the use to which it is to be put.

Gas velocities in the reaction zone at or near sonic velocities are particularly desirable in the maintainance of smooth operation. Instead of using spray nozzles to disseminate the polymer compositions in the gas stream, dissemination may be effected in other ways, as by the use of rapidly rotating members.

Among the uses of the aerosols of the invention are those dependent on the reflective or absorbent power of the aerosols for radiant energy. For example, they may be used to prevent frost damage to crops by preventing the radiation of heat from orchards and the like. They may, of course, be used for the usual purposes of presently available smokes, such as smoke screens, smoke signals and sky writing with the added advantage that due to the low density to size ratios, the smokes of the invention have low settling rates. Other uses will depend on the utilization of the dispersed polymeric particles as efficient carriers for reactive substances, such as silver iodide for cloud seeding tests, or insecticides for sanitation or crop protection.

The isolated and separated expanded particles of the present invention may be reconstituted into the smoke-like dispersions by redispersion in gaseous carriers, either in the form in which they are collected or after coating or other treatment to vary their color or reflectance for many uses.

The collected particles may be used as light-weight fillers, expanders or texturing agents in links, paints, enamels and other coating compositions, and in rubber and plastic compositions. They may also be used as fillers in paper stock or in paper coating compositions. Other uses include their application as soil conditioners, either as collected or after incorporating pesticides, plant nutrients or coloring substances, or as light-weight fillers for tires and as pourable, light-weight insulation.

The particles may be collected on a layer or coating of an adhesive or binder composition to provide useful coatings of variable texture, transparency and gloss, and useful coatings may be produced by impinging the gas stream bearing the particles on a collect-

ing surface before the particles are fully hardened.

EXAMPLE I

One hundred parts of a thermosetting partially reacted phenol-formaldehyde resin, made by heating one molar equivalent of phenol with two and one-half molar equivalents of formaldehyde, as 40 percent aqueous solution, in the presence of 0.05 molar equivalents of sodium hydroxide for two hours at about 80 to 85° C, neutralizing with lactic acid and dehydrating under vacuum to about 10 percent of water, is mixed with seven parts of isopropyl ether, and one part of a polyoxyalkylene ether of sorbitan monopalmitate as a wetting agent in one tank of the apparatus of the drawing and a catalyst composition of 50 parts of 66° Bé sulfuric acid and 7 parts of 85 percent phosphoric acid in 50 parts of water are placed in the other tank.

The compressor-turbine system is started up and adjusted to give a stream of exhaust gases at about 565° C. When the resin mixture and the catalyst composition are fed into the venturi section at the rate of about 22 parts of the catalyst composition to 100 parts of the resin mixture, a pink smoke is formed which consists of dispersed spherical cellular particles of phenolic resin.

EXAMPLE II

When furfuryl alcohol is added to the resin composition of Example I in the proportion of 10 parts of furfuryl alcohol and 6 parts of isopropyl alcohol to 84 parts of the phenol-formaldehyde resin, a black smoke is produced when injected into the hot exhaust gas stream as in Example I.

EXAMPLE III

When a two component urethane foam composition consisting, as to component A, of 78.8 parts of an isocyanate terminated polyether prepolymer and 21.2 parts of trichlorofluoromethane, and, as to component B, 66.4 parts of a polyether containing a polypropyleneoxide chain, 20.7 parts of trichlorofluoromethane and 3.3 parts of triethylamine as catalyst, is fed to the venturi section of the apparatus of the drawing as described in Example I a white smoke consisting of dispersed cellular micro particles is produced.

The trichlorofluoromethane reduces the viscosity of the liquid components and also acts as a blowing agent.

WHAT I CLAIM IS:—

1. A process for the production of an expanded, particulate organic polymeric material which comprises introducing or injecting a polymeric material or, if desired, suitable starting materials or reactants which are capable of forming such polymeric material, and which polymers or starting materials, respectively, are, due to their composition or due to the presence of a suitable adjuvant, cap-

able of foaming or expanding at an elevated temperature, into a stream of a hot gas which has a temperature high enough to initiate the foaming or expansion of the polymeric material introduced or formed, and a velocity which is close to or higher than sonic velocity.

2. A process in accordance with claim 1, in which the rate of travel of the gas stream is increased, at or close to the point where the reactants or the polymeric material are introduced into the gas stream.

3. Process in accordance with claim 1 or claim 2, in which the gas stream is given a high rate of turbulence, particularly at the point where the reactants or the polymeric materials are introduced.

4. Process in accordance with any one of claims 1 to 3, in which there is employed as the starting material a polymeric material which contains a suitable blowing agent.

5. Process in accordance with claim 4, in which there is employed a blowing agent which is effective by thermo-decomposition with the formation of gaseous decomposition products.

6. Process in accordance with claim 4, in which there is employed as the blowing agent a gas, vapor or a volatile liquid which is effective by thermal expansion.

7. Process in accordance with any one of claims 1 to 6, in which the polymeric material is capable of hardening or curing in the expanded form by the effect of the high temperatures employed in the process.

8. Process in accordance with claim 1 or claim 2, in which are employed as the starting material, reactants which unite to form the polymeric material with the formation of vapors or gases.

9. Process in accordance with claim 8, in which are employed as the starting material reactants which are capable of forming a foamed polyurethane.

10. Process in accordance with any one of claims 1 to 9, in which the gas stream producing the expanded polymer particles is directly blown into space or into the atmosphere to form a stable smoke or fog.

11. Process in accordance with any one of claims 1 to 10 in which the expanded particles of polymer serve as a carrier for the distribution of biologically active materials such as insecticides.

12. Process in accordance with any one of claims 1 to 11, in which the size and density of the particles is controlled by varying the temperature or the velocity of the hot gas stream or both the temperature and the velocity of the gas stream.

13. Process in accordance with any one of claims 1 to 12, in which the size and density of the particles is furthermore controlled by the selection of the blowing agent and by adjusting the ratio of blowing agent to polymeric material.

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14. Process in accordance with any one of claims 1 to 13, in which the polymeric material is injected, as one or several independent streams, into the hot gas stream in the form of a liquid, melt or a solution of the polymeric material in a volatile organic liquid. 65
15. Process in accordance with any one of claims 1 to 14, in which the components capable of reacting with the formation of a polymeric material are injected into the hot gas stream separately as individual streams. 70
16. Process in accordance with any one of claims 1 to 15, in which the polymeric material containing a suitable blowing agent is introduced into the hot gas stream in the form of fine solid particles. 75
17. Process in accordance with claim 16, in which the fine solid particles of the polymeric material are dispersed in a gaseous or liquid carrier material. 80
18. Process in accordance with any one of claims 1 to 17, in which the hot gas stream is generated in a gas turbine, including portable gas turbines or similar devices. 85
19. Powdered organic polymeric material which is produced by the process claimed in claim 1 and is characterized in that the individual particles are expanded open or closed cell micro particles with a size of between 1 micron and 1,000 microns. 90
20. Powdered organic polymeric material in accordance with claim 19, characterized in that the individual particles are expanded multicellular particles wherein each cell has a diameter of not more than 1,000 microns and preferably less than 100 microns. 95
21. Powdered material in accordance with claim 19 or claim 20, which consists of or contains a thermoplastic polymeric material. 100
22. Powdered material in accordance with claim 19 or claim 20, which consists of or contains a thermosetting polymeric material. 105
23. Powdered material in accordance with claim 21, which consists of or contains as the thermoplastic polymeric material at least one addition polymer. 110
24. Powdered material in accordance with claim 19 or claim 20, which consists of or contains one or more of urea-formaldehyde polymers, phenol-formaldehyde condensation products, polyurethane resins, epoxy resins or silicone resins. 115
25. Powdered material in accordance with any one of claims 19 to 24, in which the closed cells or units of cells contain a fugacious substance. 120
26. Powdered material in accordance with claim 25, in which the fugacious substance is a gas.
27. Powdered material in accordance with claim 26, in which the gas is air, hydrogen, carbon dioxide or helium.
28. Powdered material in accordance with any one of claims 18 to 24, in which the closed cells or units of cells contain a vapor. 65
29. Powdered material in accordance with claim 28, in which the closed cells or units of cells contain the vapor of at least one of water, acetone, methyl chloride or other halogenated lower hydrocarbons. 70
30. Powdered material in accordance with any one of claims 19 to 29, which contains as fillers or additives pigments or finely divided metal particles. 75
31. Powdered material in accordance with claim 30, in which the fillers or additives are finely divided and dispersed in the polymer making up the cell walls. 80
32. Powdered material in accordance with any one of claims 19 to 31, in which the polymeric expanded particles have a density which is substantially below 1 g/c cm. 85
33. Powdered material in accordance with any one of claims 19 to 32, in which the particles have a density corresponding approximately to that of air. 90
34. Powdered material in accordance with any one of claims 19 to 33, which is dispersed in a gas or in air forming a fog or smoke having a low settling rate. 95
35. Apparatus for carrying out the process of claims 1 to 18, which comprises a compressor and a turbine on the same shaft therewith, a combustion chamber, conduits connecting the compressor, combustion chamber and the turbine in this order, designed to forward and heat the compressed gas and a venturi connected to the exit side of the turbine, and one or more inlets protruding into the venturi passage, which inlets are connected with means for supplying the liquid or solid polymeric materials or the starting material therefor. 100
36. Process for the production of particulate expanded polymeric material substantially as hereinbefore described. 105
37. Process for the production of particulate expanded polymeric material substantially as described with reference to the specific Examples. 110
38. Expanded polymeric material whenever produced by the process claimed in any one of claims 1 to 18, 36 or 37. 115
39. Apparatus suitable for the production of particulate expanded polymeric material substantially as described with reference to the accompanying drawing. 120
40. Powdered organic polymeric material whenever produced by the apparatus claimed in either of claims 35 or 39.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

